

## Unit 1: Structure and Bonding Models

### Planck's Quantum Theory:

Electromagnetic wave theory could not explain the phenomena of photoelectric effect and black body radiations. Max Planck (1900) put forward a theory known as quantum theory of radiation in order to explain these phenomena. The main features of Planck's quantum theory are,

- The radiant energy is not emitted or absorbed continuously but discontinuously in the form of small packets of energy called quantum. The quantum energy of light is termed as photon.
- The energy associated with each quantum is directly proportional to the frequency of the radiation

Mathematically,

$$E \propto \nu$$

$$E = h\nu$$

Where E = energy of the photon

$\nu$  = frequency of the radiation

$h$  = Planck's constant ( $6.626 \times 10^{-27}$  erg sec or  $6.626 \times 10^{-34}$  Joules sec)

- The total amount of energy emitted or absorbed by a body will be some whole number multiple of quantum by an integer 'n'

$$E = nh\nu \text{ where } n=1, 2, 3 \dots$$

Similarly

$$E = \frac{hc}{\lambda} \quad (\because \nu = \frac{c}{\lambda})$$

- The above equation says that a wave of higher frequency or lower wavelength will be more energetic and vice versa. For example, the violet light of high frequency has more energy whereas red light of low frequency will exhibit less energy

### Dual Nature of the Matter (de Broglie equation):

- Electrons behave both as particles and waves. This type of dual behavior is also exhibited by light and even atoms.
- For example, in a discharge tube, electrons behave as particles, whereas in electron diffraction experiments, they act as electromagnetic waves.
- Phenomena such as photoelectric effect, reflection, and refraction of light can be explained on the basis of the particle nature of light, whereas the common phenomena of interference and diffraction can be explained by the wave theory of light.

- Thus, light (like electrons) is considered to have a dual nature as a particle and as a wave. This joint particle and wave character of matter and radiation is called wave-particle duality.
- Louis de Broglie suggested that dual nature (wave and particle) should not be confined to radiations alone but should also be extended to matter.
- Bohr's theory treats the electron exclusively as a particle.
- According to de Broglie, however, every material particle such as an electron should have not only the particle properties but also the wave properties.
- He proposed a relation between momentum and wavelength of a particle in motion.

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$

Where,  $h$  = Planck's constant

$P$  = Momentum

$\lambda$  = Wavelength

$m$  = Mass of electron

$v$  = Velocity of moving electron

This is known as de Broglie's equation, which is derived as follows:

$$E = h\nu \quad (\text{Planck's relation for energy of radiation})$$

$$E = mc^2 \quad (\text{Einstein's relation for motion of particles})$$

Combining the two equations,

$$h\nu = mc^2 \quad [c = \text{Velocity of light}]$$

$$\frac{hc}{\lambda} = mc^2$$

$$\frac{h}{\lambda} = mc$$

$$\lambda = \frac{h}{mc} = \frac{h}{mv} \quad \text{where } c \text{ replace by } v$$

Now momentum  $P = mv$

$$\lambda = \frac{h}{P}$$

- The velocity ' $v$ ' (a particle property) is thus connected to wavelength  $\lambda$  (a wave property) by Planck's constant

- de Broglie's concept is significant only for small particles (such as an electron) and insignificant for large particles (such as a baseball).

### Heisenberg's Uncertainty Principle:

Heisenberg's Uncertainty Principle states that "It is impossible to know exactly both the position and the momentum of an electron or any other microscopic particle simultaneously with accuracy".

Mathematically

$$\Delta x \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x m \Delta v \geq \frac{h}{4\pi}$$

Where  $\Delta x$  = uncertainty in position

$\Delta p$  = uncertainty in momentum i.e.,  $m\Delta v$

$h$  = Planck constant

$m$  = mass of electron

If the position of the particle is known exactly ( $\Delta x = 0$ ), then  $\Delta v$  become infinity and vice versa.

**Case.1.** If the position of the particle known exactly ( $\Delta x = 0$ ), then

$$\Delta x \Delta v = \frac{h}{4\pi m}$$

$$\Delta v = \frac{h}{4\pi m \Delta x} = \frac{h}{4\pi m 0} = \infty$$

**Case.2.** If the velocity of the particle is known exactly ( $\Delta v = 0$ ), then

$$\Delta x \Delta v = \frac{h}{4\pi m}$$

$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{h}{4\pi m 0} = \infty$$

The uncertainty principle has no significance for macromolecules. The uncertainty principle which gives the wave nature of the electron only provides the probability of finding the electron in a given space. Therefore, the classical concept of Bohr's model of the atom has been replaced by probabilities approach.

## Schrodinger Equation:

In 1926, Erwin Schrodinger developed a new model of the atom. He incorporated the idea of quantization and the conclusion of de Broglie's hypothesis and Heisenberg's uncertainty principle in this model. In the Schrodinger wave equation, electrons are treated as a wave motion in three-dimensional space around the nucleus having nodes and quantized energies. From the classical wave mechanics, if  $\psi$  (psi) is the amplitude or wave function of a wave moving in a three-dimensional space with a velocity of  $v$  and frequency  $\nu$ , the wave equation is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 \nu^2 \psi = 0$$

According to non-classical de-Broglie's equation

$$\lambda = \frac{h}{mv} \quad \text{Where } v = \nu \lambda$$

$$\frac{1}{\lambda} = \frac{mv}{h} = \frac{\nu}{v}$$

Substituting in the Eq. (3)

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 \left( \frac{mv}{h} \right)^2 \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 \frac{m^2 v^2}{h^2} \psi = 0$$

But kinetic energy  $K.E = \frac{1}{2}mv^2$  or  $m^2 v^2 = 2m K.E$ . Substituting in Eq. (4)

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m K.E}{h^2} \psi = 0$$

But the total energy  $E = K.E. + P.E.$

Hence,  $K.E. = E - P.E. (V)$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

$$\text{Or simply } \nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

This is known as the Schrodinger equation, where

$$\nabla^2 = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \text{ Called the Laplace operator.}$$

Here,  $m$  = mass of the electron,  $V$  = potential energy (PE.),  $E$  = total energy,  $h$  = Planck's constant

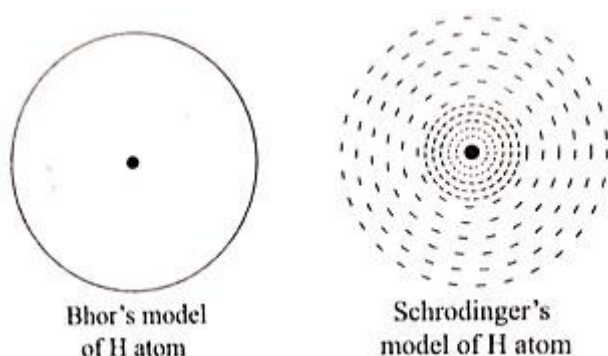
$x, y, z$  are the Cartesian coordinates in the three-dimensional space.

### **Significance of $\Psi$ and $\Psi^2$ :**

$\Psi$  is the amplitude (maximum displacement) of the wave and is called the wave function. It takes a positive value above the axis and negative value below the axis and becomes zero while crossing/intercepting the axis.  $\Psi$  is a state function but it has no physical significance, it only represents the amplitude of electron wave. The square of  $\Psi$  at a point gives the probability function, which describes the probability of finding an electron around the nucleus, and the point where the value of  $\Psi^2$  is maximum is called the orbital. The value of  $\Psi^2$  is always positive. From the value of  $\Psi^2$  at different points within the atom, it is possible to find out the orbital of the electron. Evidently,  $\Psi^2$  can be interpreted as a probability density. If  $dv$  is definite volume, then  $\Psi^2 dv$  gives the probability of finding the electron in the region having a volume  $dv$ .

### **Application of Schrodinger Equation to Hydrogen Atom**

When a matter wave is exhibiting exclusive wave nature, in classical wave mechanics,  $\Psi$  represents the amplitude, and the square of the amplitude ( $\Psi^2$ ) gives the intensity of the light. When the matter-wave has exclusive particle character,  $\Psi^2$  can be said to represent the density of particles. But if you consider a case like a hydrogen atom where a single electron revolves around the nucleus, the issue of the density of particles is meaningless and  $\Psi^2$  speaks about the probability of finding an electron at a particular place. To understand the complete space distribution of an electron we must understand the total probability or electron density of an electron. Consider the revolution of an electron present in the K shell of the hydrogen atom (Fig).



From above Fig., we find that the electron density or probability of finding an electron is very high near the nucleus, but this probability decreases as we move further away from the nucleus. Schrodinger solved the wave equation for hydrogen and some other simple atoms and actually obtained a set of wave functions that describe allowed energies and shapes of electron waves. Each of these different possible waves is called an orbital. Each orbital has a fixed amount of energy and describes a probability where the electron could be found.

## MOLECULAR ORBITAL THEORY

Valence Bond Theory fails to answer certain questions like Why  $\text{He}_2$  molecule does not exist and why  $\text{O}_2$  is paramagnetic? Therefore in 1932 F. Hund and R.S. Mulliken came up with theory known as **Molecular Orbital Theory** to explain questions like above. The salient features of this theory are:

- The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
- The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called anti-bonding molecular orbital.
- The bonding molecular orbital has lower energy and hence greater stability than the corresponding anti-bonding molecular orbital.
- Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
- The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle and the Hund's rule

### Linear Combination of Atomic Orbitals (LCAO)

Linear Combination (addition or subtraction) of atomic orbitals which combine to form molecule. Consider two atoms A and B which have atomic orbitals described by the wave functions  $\Psi_A$  and  $\Psi_B$ . If electron cloud of these two atoms overlap, then the wave

function for the molecule can be obtained by a linear combination of the atomic orbitals  $\Psi_A$  and  $\Psi_B$  i.e. by subtraction or addition of wave functions of atomic orbitals

$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

The above equation forms two molecular orbitals

### Bonding Molecular Orbitals

When addition of wave function takes place, the type of molecular orbitals formed are called Bonding Molecular orbitals and is represented by

$$\Psi_{MO} = \Psi_A + \Psi_B$$

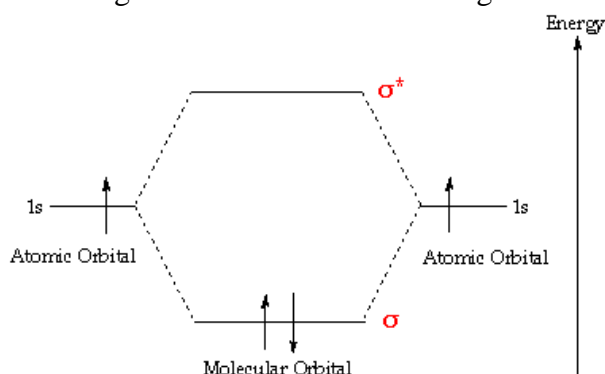
They have lower energy than atomic orbitals involved. It is similar to **constructive interference occurring in phase** because of which electron probability density increases resulting in formation of bonding orbital.

### Anti-Bonding Molecular Orbitals

When molecular orbital is formed by subtraction of wave function, the type of molecular orbitals formed are called Antibonding Molecular Orbitals and is represented by

$$\Psi_{MO} = \Psi_A - \Psi_B$$

They have higher energy than atomic orbitals. It is similar to **destructive interference occurring out of phase** resulting in formation of antibonding orbitals.



Therefore, Combination of two atomic orbitals results in formation of two molecular orbitals, bonding molecular orbital (BMO) whereas other is anti-bonding molecular orbital (ABMO). Therefore, a molecular orbital is polycentric and atomic orbital is monocentric. Number of molecular orbitals formed is equal to the number of atomic orbitals.

### Energies of Molecular Orbitals

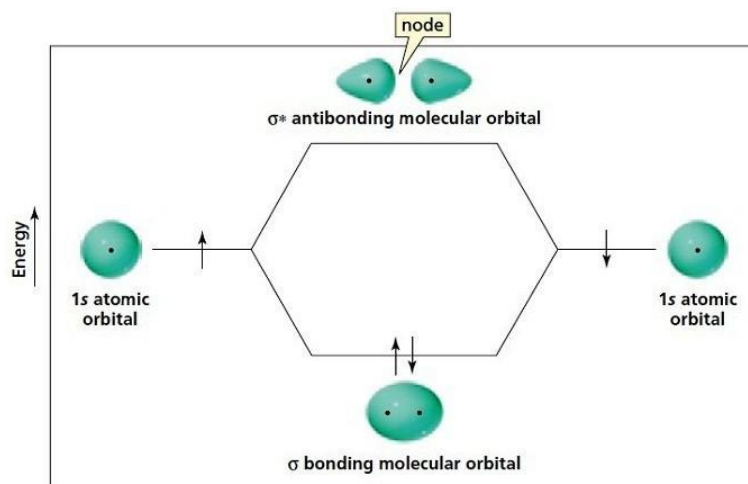
#### Bonding Molecular Orbitals (BMO):

Energy of Bonding Molecular Orbitals is less than that of Anti Bonding Molecular Orbitals because the attraction of both the nuclei for both the electron (of the combining atom) is increased.

#### Anti-Bonding Molecular Orbitals (ABMO):

Energy of Anti Bonding Molecular Orbitals is higher than Bonding Molecular Orbitals because the electrons try to move away from the nuclei and are in repulsive state.

The Energies of Bonding Molecular Orbitals and Anti-Bonding Molecular Orbitals are shown in figure below:



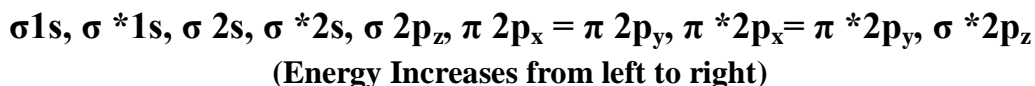
### Rules for Filling of Molecular Orbitals:

Certain rules are to be followed while filling up molecular orbitals with electrons in order to write correct molecular configurations:

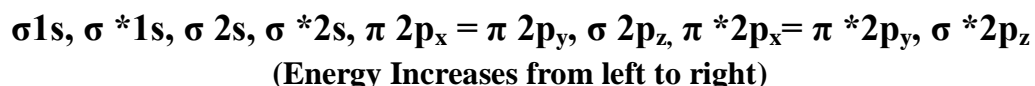
1. **Aufbau Principle** – This principle states that those molecular orbital which have the lowest energy are filled first.
2. **Pauli's Exclusion Principle** – According to this principle each molecular orbital can accommodate maximum of two electrons having opposite spins.
3. **Hund's Rule** – This rule states that in two molecular orbitals of the same energy, the pairing of electrons will occur when each orbital of same energy consist one electron.

### Energy Level Diagram for various molecules

The molecular orbital configuration for **homonuclear diatomic molecules** is below,



The molecular orbital configuration for **heteronuclear diatomic molecules** is below,



### Bond Order:

It may be defined as the half of difference between the number of electrons present in the bonding orbitals and the antibonding orbitals that is,

$$\text{Bond order (B.O.)} = \frac{1}{2} (\text{No. of electrons in BMO} - \text{No. of electrons in ABMO})$$

Those with positive bonding order are considered stable molecule while those with negative bond order or zero bond order are unstable molecule.

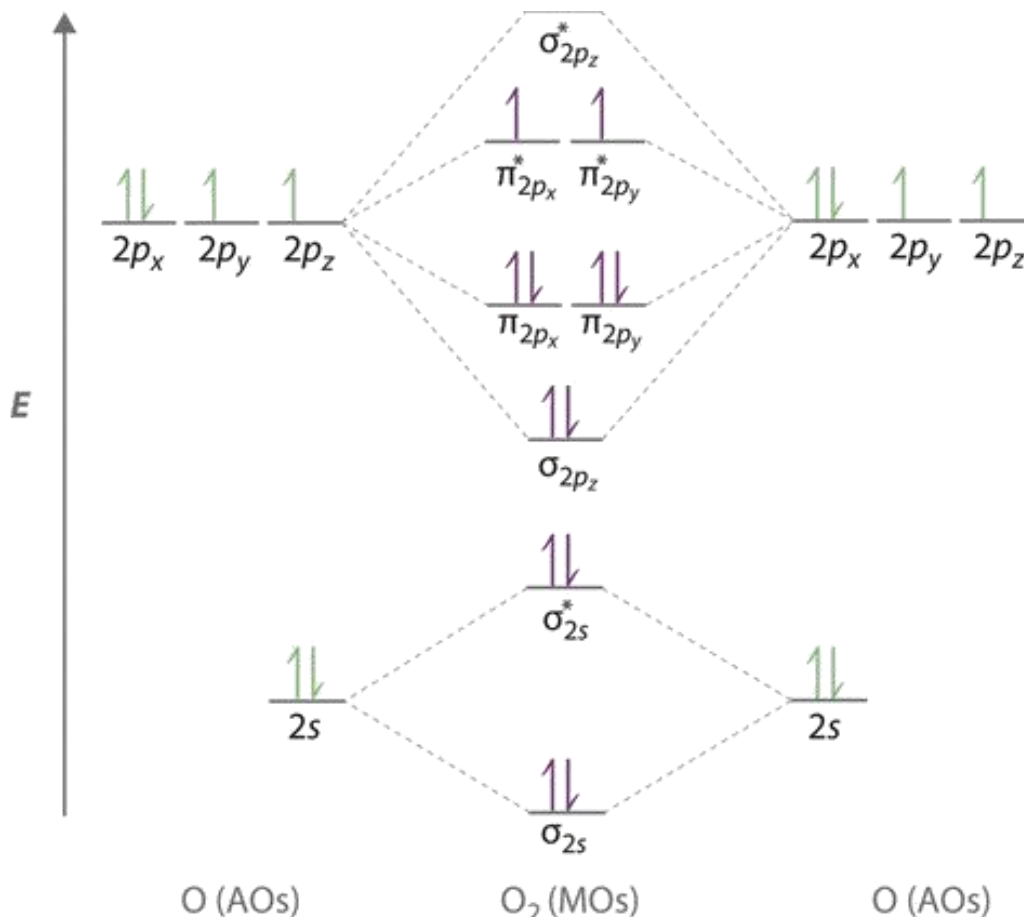
### Magnetic Behavior:

If all the molecular orbitals in species are spin paired, the substance is diamagnetic. But if one or more molecular orbitals are singly occupied it is paramagnetic.



### Molecular orbital energy level diagram of Oxygen molecule (O<sub>2</sub>):

Oxygen atom has electronic configuration of  $1s^2 2s^2 2p^4$ . Therefore, oxygen molecule has 16 electrons. In the formation of molecular orbitals, the electrons in the inner shells are expressed as KK denoting  $\sigma 1s^2$ ,  $\sigma^* 1s^2$ . The remaining 12 electrons are filled in molecular orbitals as shown below



For O<sub>2</sub>

The electronic configuration of O<sub>2</sub> molecule is  $KK\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$

Bond Order =  $\frac{8-4}{2} = 2$

Thus, O<sub>2</sub> contains a double bond. O–O bond length is  $1.2\text{\AA}$ , and the bond energy is 498.4 kJ/mol and paramagnetic nature due to presence of lone paired of electrons.

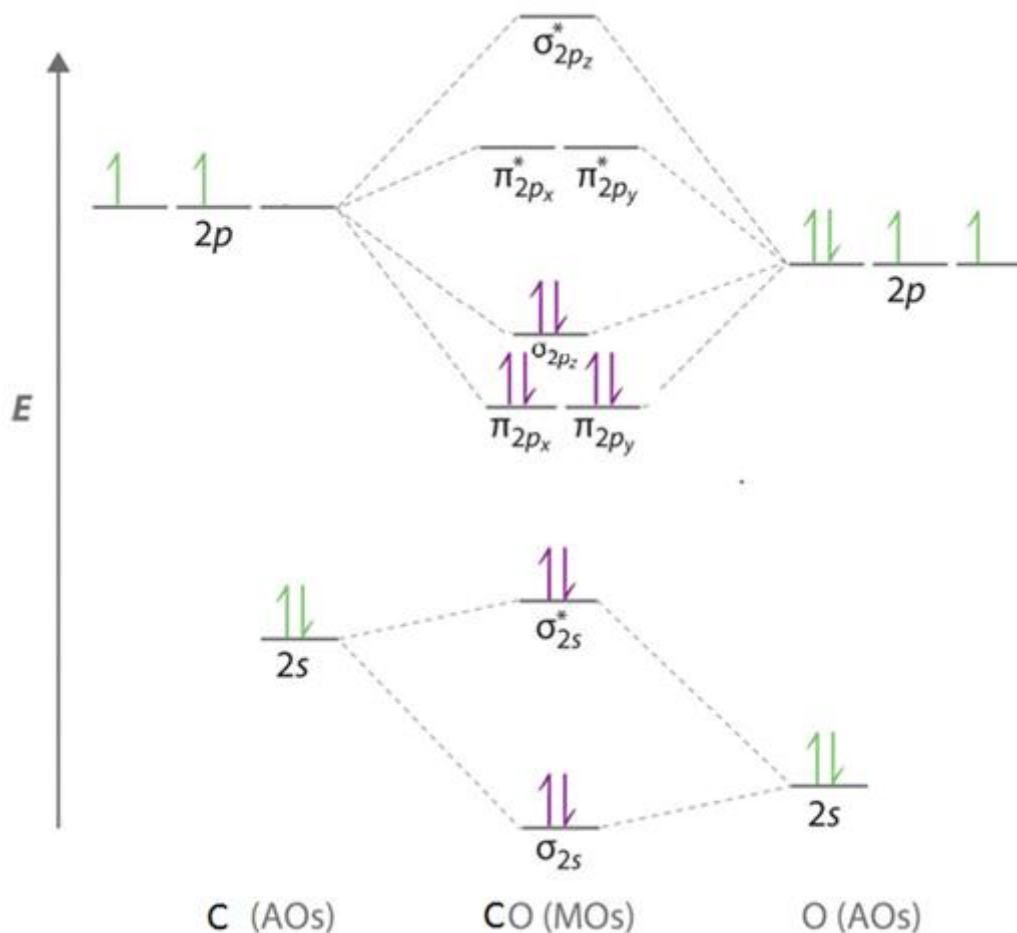
### Molecular orbital energy level diagram of carbon monoxide molecule (CO):

The electronic configurations of carbon and oxygen atom are  $1s^2 2s^2 2p^2$  and  $1s^2 2s^2 2p^4$  respectively. There are 4 electrons in the outer shell of carbon and 6 electrons in the outer shell of oxygen. Thus, the totals of 10 outer electrons are to be accommodated in the molecular orbitals of CO molecule. Because of higher electro negativity of oxygen, its atomic orbitals would be of lower energy than the corresponding atomic orbitals of carbon.

The electronic configuration of CO molecule is  $KK\sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$

$$\text{Bond order} = 1/2(8-2) = 3$$

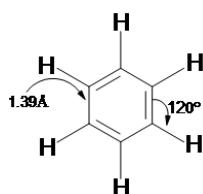
Thus, CO contains a triple bond. Its bond dissociation energy is 1067 KJ/mol and bond length is equal to 1.14 Å. Molecular orbital diagram for CO molecule is given as.



### $\pi$ Molecular Orbitals of Benzene:

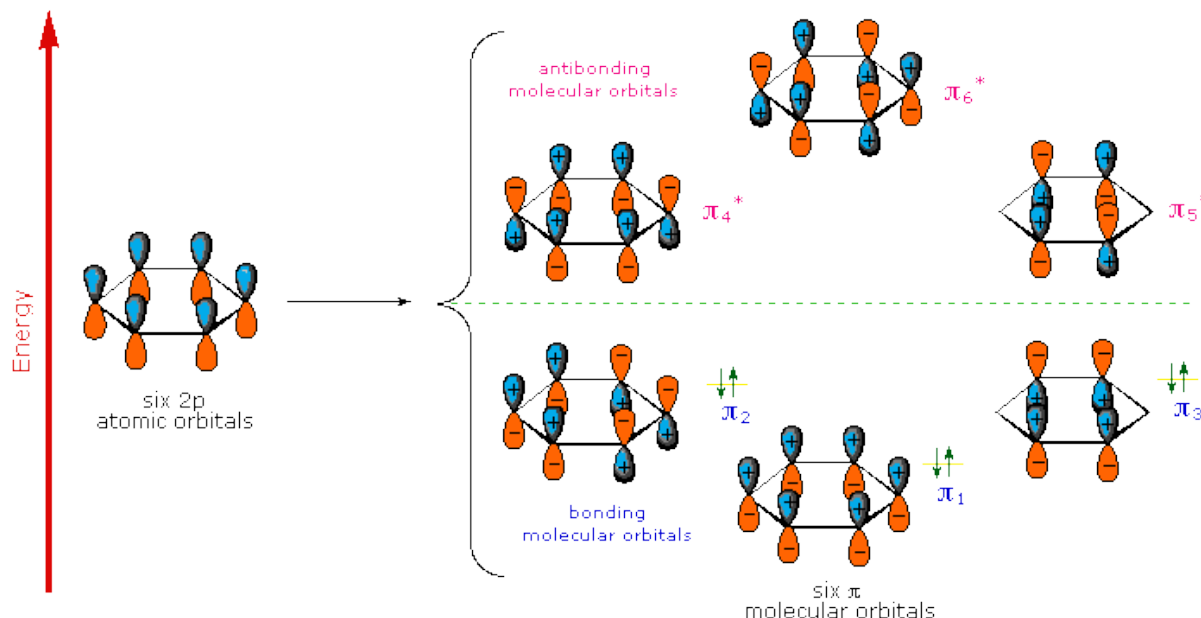
Benzene is a planar molecule containing a ring of six carbon atoms, each with a hydrogen atom attached. All of the carbon-carbon bonds have exactly the same lengths having single and double bonds. There are delocalized electrons above and below the plane of the ring.

There are a total of six p-orbital electrons that form the stabilizing electron clouds above and below the aromatic ring.



### Molecular Orbital description:

We know that benzene has a planar hexagonal structure in which all the carbon atoms are  $sp^2$  hybridized, and all the carbon-carbon bonds are equal in length. As shown below, the remaining cyclic array of six p-orbitals (one on each carbon) overlap to generate six molecular orbitals, three bonding and three antibonding.

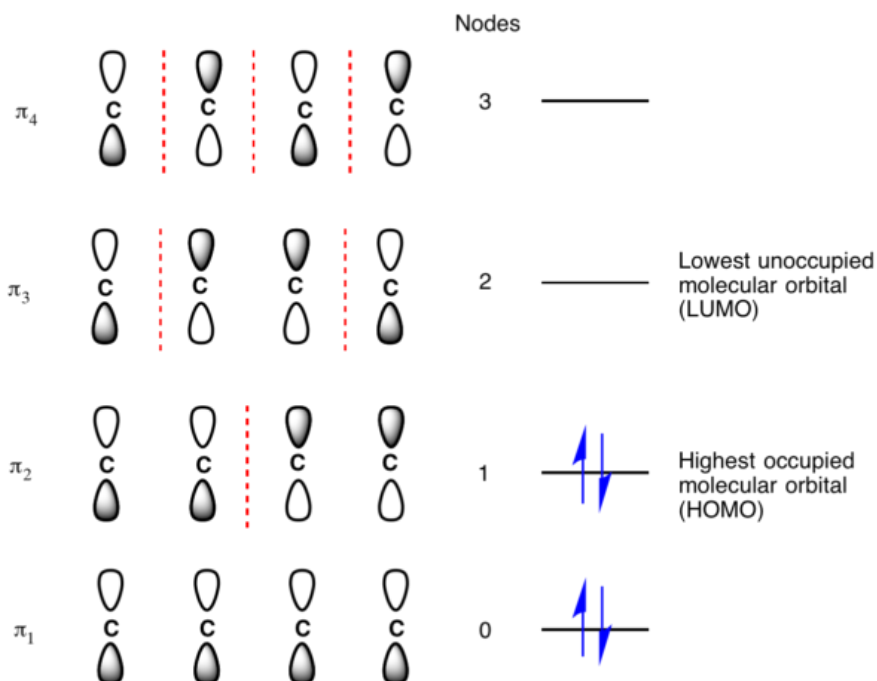


The plus and minus signs shown in the diagram do not represent electrostatic charge, but refer to phase signs. When the phases correspond, the orbitals overlap to generate a common region of like phase, with those orbitals having the greatest overlap (e.g.  $\pi_1$ ) being lowest in energy. The remaining carbon valence electrons then occupy these molecular orbitals in pairs, resulting in a fully occupied (6 electrons) set of bonding molecular orbitals.

### $\pi$ Molecular Orbitals of Butadiene:

Butadiene is composed of 4 carbons with two adjacent pi bonds. these two pi bonds are conjugated : all four p orbitals are all aligned with each other, and build up into a larger pi system. Since butadiene consists of 4 individual p orbitals, the pi-system of butadiene will contain 4 pi molecular orbitals. It has two double bonds with two electrons each, for a total of 4 pi electrons. We fill up the lowest-energy molecular orbitals first, which gives us the following

### Molecular Orbital Diagram for Butadiene



The molecular orbital diagram of Butadiene shows two molecular orbitals.

1. **Highest Occupied Molecular Orbital (HOMO)**
2. **Lowest Unoccupied Molecular Orbital (LUMO)**

The **highest occupied molecular orbital (HOMO)** is  $\pi_2$ . It is the “valence electrons” of the pi system and most readily lost. If butadiene participates in a reaction where it is the electron-donor (nucleophile), its electrons are going to come from that orbital.

The **lowest unoccupied molecular orbital (LUMO)** is  $\pi_3$ . The LUMO is the lowest-energy unoccupied orbital. If butadiene participates in a reaction where it is the electron acceptor (electrophile), the electrons will be donated to that orbital.